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STUDY OF ULTRASONIC VELOCITY IN LIQUIDS

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(*Received January* 11, 1961)

ABSTRACT. Ultrasonic velocity measurements are carried out in a number of new organic liquids, low melting point organic solids in the molten state and corrosive inorganic liquids. The important constants adiabatic compressibility, β_{ad}, γ, C_v, Van der Waals' "b" and molecular radii are computed. A method different from that of Schaaffs was followed in computing the value of "b" for atoms and linkages and the values for some atoms and linkages are obtained. It is found that the contribution of semipolar bond to Van der Waals' "b" is negative.

INTRODUCTION

Extensive studies of ultrasonic velocity in liquids and their interpretation in the light of molecular structure have been made by several investigators like Parthasarathy (1935, 1936, 1937), Schaaffs (1945, 1950, 1951), Baccaredda and Giacomini (1945, 1946, 1947, 1949, 1950), Lagemann (1948, 1953, 1957), Rao and others (1940, 1941). An important advance has been made when Rao (1941) has discovered R the molar sound velocity, a temperature independent constant and it is characteristic of the atoms and linkages in a molecule. Schaaffs (1957) has shown that the measurement of ultrasonic velocity enables the computation of certain thermodynamic constants such as β_{ad} and C_v and the molecular constants as Van der Waals' "b" and molecular radii. It has already been established by many workers that Van der Waals' "b" is an additive function of the atoms and linkages as some other physical properties like parachor "P" critical volume "Vc" etc. Schaaffs (1950) has given values of b for various elementary groups and atoms with different linkages. He tested the validity of this additive law in some compounds and obtained a good agreement between the calculated and experimental values of "b" as well as ultrasonic velocity "V".

In the present investigation the authors presented the ultrasonic velocity data and the various thermodynamic constants for many new liquids. An attempt is made to compute the value of Van der Waals' "b" for atoms and various linkages by following a method different from that of Schaaffs and it is tested in many common organic liquids for which the ultrasonic velocity data are available.

RESULTS

The ultrasonic velocity data along with the various constants calculated for the liquids studied are presented in Table I. The ultrasonic velocities for the

TABLE I

Compound	Temp °C	Velocity m/s V	β_{ad} X 10 cm2/ dyne	Ratio of specific heat	C_v	rX10⁸ cm	r from
Diethylamine	23.5	1103	118.00	1.149	1.8870	2.142	2.133 (27.5°C)
Isopropylamine	20.0	1089	123.50	—	—	1.994	1.998 (27.5°C)
Dimethyl sulphate	31.0	1223	50.74	—	—	2.075	2.018 (27.0°C)
Diethyl sulphate	31.2	1199	59.17	—	—	2.310	2.320
Sulphur chloride	26.0	1173	43.57	2.187	0.4211	1.956	2.272 (20.8°C)
Thionyl chloride	30.6	1023	58.86	2.197	0.4610	1.894	2.061 (10.0°C)
Sulphuryl chloride	30.6	925	70.50	1.877	0.5194	1.961	2.041 (20.0°C)
Triethyl phosphate	30.6	1226	62.59	—	—	2.513	2.811 (27.5°C)
Triphenyl phosphate	58.0	1385	43.33	—	—	2.961	3.239 (55.0°C)
Azoxy benzene	29.9	1532	36.43	—	—	2.530	2.922 (27.5°C)
Azo benzene	67.7	1355	52.29	1.299	1.0620	2.538	—
Vinyl acetate	25.7	1122	85.88	—	—	1.783	1.809 (27.0°C)
Methyl methacrylate	29.7	1179	76.58	—	—	2.140	2.186
Ethyl methacrylate	25.0	1180	78.57	—	—	2.258	2.309
Naphthalene	89.6	1183	73.07	1.317	0.3045	2.294	2.403 (99.0°C)
Diphenyl	74.8	1361	54.69	—	—	2.466	2.746 (78.0°C)
Phenyl salicylate	69.8	1336	48.34	1.232	1.3280	2.592	2.885 (48.0°C)
Maleic anhydride	86.2	1433	35.91	—	—	1.893	—
Phenol	64.6	1396	49.49	1.237	1.8920	2.354	2.220 (45.0°C)
p-dichloro benzene	67.7	1118	64.83	1.487	0.8390	2.227	2.437 (56.0°C)
Antimony trichloride	100.0	88.8	38.59	—	—	1.997	—
Sodium acetate	90.0	1701	27.10	—	—		

TABLE II

Temperature 20°C

Compound	Formula	Experimental value of "b"	Computed value of "b"
Nonane	C_9H_{20}	164.60	161.70
Ethyl alcohol	C_2H_5OH	52.46	52.08
Propyl alcohol	C_3H_7OH	64.62	67.51
Pentachloro ethane	$C_2H_5Cl_5$	127.20	122.00
Tetrachloro ethane	$C_2H_2Cl_4$	99.65	106.20
Carbon tetrachloride	CCl_4	90.63	90.79
Amyl bromide	$C_5H_{11}Br$	116.10	108.20
Bromoform	$CHBr_3$	83.03	84.08
Tetrabromo ethane	$C_2H_2Br_4$	111.90	118.50
Propyl iodide	C_3H_7I	91.52	88.77
Ethyl iodide	C_2H_5I	75.08	73.34
Chloro benzene	C_6H_5Cl	96.23	95.67
Orthochloro toluene	$C_6H_5CH_2Cl$	122.80	111.10
Toluene	$C_6H_5CH_3$	100.30	95.38

Table III

Values of Van der Waals' 'b' for some atoms and linkages

C = 3.23		
H = 6.11		
N = 16.14		
Cl = 21.89	(=) in (C=O)	= 12.55
Br = 24.95	(=) i (C=C)	= 24.05
I = 36.38	(=)	= 8.11
S = 17.50	Benzene ring	= 23.90
P = 15.95		
Sb = 12.71		
O = 9.02		

TABLE IV

Temperature 20° C

Compound	Velocity (m/sec) V	Density (gm/cc)	Experimental value of "b"	Computed value of "b"
* Diethylamine	1150	0.7071	96.16	96.16
Isopropylamine	1089	0.6836	79.69	81.73
* Dimethyl sulphate	1255	1.333	89.82	89.82
Diethyl sulphate	1244	1.188	123.30	121.38
* Sulphur chloride	1198	1.622	78.79	78.79
Thionyl chloride	1148	1.839	60.94	65.59
Sulphuryl chloride	940	1.673	75.48	75.91
Ethyl phosphate	1219	1.074	152.40	158.90
Triphenyl phosphate	1510	1.236	184.90	269.30
Azo benzene	1494	1.083	161.70	203.90
Azoxy benzene	1558	1.180	161.90	208.90
Vinyl acetate.	1152	0.9315	96.36	104.16
Methyl methacrylate	1220	0.949	99.19	119.59
Ethyl methacrylate	1201.5	0.919	117.00	134.80
Naphthalene.	1392	1.030	118.50	132.80
Diphenyl	1534	1.035	149.00	147.60
Phenyl salicylate	1489	1.196	172.50	190.40
Phenol	1528	1.079	82.77	88.90
p-dichloro benzene	1252	1.292	108.10	110.50
* Antimony trichloride.	1128	2.780	78.38	78.38
* Phosphorus trichloride	995	1.580	81.62	81.62

*These liquids have been taken for standardization.

organic liquids and the low melting point organic solids are measured by the fixed path variable frequency interferometer. The corrosive liquids are studied with a special type of all glass cell using pulse techniques. The glass cell is made by fusing two parallel ground glass plates to the two ends of a cylindrical tube. The length of the cell is about 4.5 cms. The crystals are attached to the two sides of the cell. The liquids used are of E. Merck samples. The densities are determined by a specific gravity bottle. The physical constants, specific heat and thermal expansion required in computing the constants C_V, γ are taken from

International Critical Tables. As the measurements reported in Table I are made at different temperatures, the ultrasonic velocities in all the different substances are reduced to the same temperature of 20°C to facilitate comparison by using the known temperature variation data obtained by the authors. The results thus obtained are presented in Table IV along with Van der Waals' "b" and density.

It may be noticed that there are some low melting point solids in which the ultrasonic velocity is measured in the liquid state at temperature above the melting point. The values of ultrasonic velocity given for these substances extrapolated to 20°C represent hypothetical values which these substances would have had if they exist in liquid state at 20°C.

DISCUSSION

The velocity data represented in Table IV follows well the rules proposed by Parthasarathy (1935, 1936, 1937) and Schaaffs (1948). After a detailed study of the ultrasonic velocity data available in the liquid state the authors also arrived at the general conclusion that in the homologous or progressive series of organic molecules the ultrasonic velocity varies in the same sense as the density, i.e., increasing with increase in density or decreasing with decrease in density progressively for higher members. The compressibility variation is exactly opposite. Exceptions to this rule are found in the series involving either a halogen atom or a lighter group (COOH, CH_3, etc).

Examining the velocity data in the light of the rules proposed by Parthasarathy (1937), Schaaffs (1950) and by the authors it is seen that the velocity is higher and the compressibility is lower in diethylamine than that in isopropylamine which has less chain length. Ultrasonic velocities in the monomers, methyl methacrylate and ethyl methacrylate also show a decrease for the higher member along with a decrease in density and this feature is also similar and in agreement with the general rule. The compounds ethyl sulphate and methyl sulphte also follow the same rule, though the acid radical is inorganic.

The interesting result which the authors obtained from a study of the sulphur compounds, $SOCl_2$, SO_2Cl_2 is that the presence of a semipolar double bond reduces the ultrasonic velocity. This is confirmed when we remember the fact that the contribution of semipolar double bond to molar sound velocity is negative. The high velocities of maleic anhydride and phenol may be attributed to the presence of hydroxyl groups which enhance the velocity according to Parthasarathy (1937). Comparison of measurements for the two phosphates involves an aliphatic and an aromatic compound. The triphenyl phosphate has a high molecular weight and higher density than triethyl phosphate. Besides it has the contribution of three benezene rings whose presence always increases the velocity; on both these considerations the ultrasonic velocity in triphenyl phosphate is higher than that in triethyl phosphate. A study of the structures of the two compounds azobenzene

and azoxybenzene reveals that the azoxybenzene contains one additional oxygen atom besides a semipolar bond. It is known that the effect of addition of an atom or an increase of molecular weight is generally to increase the velocity while the semipolar bond has the effect of decreasing the velocity. As the ultrasonic velocity increases for the latter accompanied by an increase of density it appears that the increase of velocity due to addition of oxygen atom is greater than the negative effect of the semipolar bond. Again the parallel increase of density and velocity and the decrease of compressibility for the higher member is in accordance with the general rule of velocity variation with density given by the author.

Comparing the velocities of naphthalene, diphenyl and phenyl salicylate, the diphenyl is a longer molecule with high molecular weight and density than naphthalene and this again leads to further increase in velocity and decrease in compressibility. Phenyl salicylate shows a departure from this behaviour and it has not been possible to explain this variation.

Phenol and paradichlorobenzene are substitution compounds of benzene and it will be appropriate to compare the velocities of the three substances at 20°C. The velocity of phenol is greater than that in benzene due to the presence of the hydroxyl group and the velocity of *p*-dichlorobenzene is less than that in benzene due to the presence of two chlorine atoms.

It is well known that the ratio of specific heats generally lies between 1 and 1.5 for all the organic liquids. In the present investigation the range of the values computed for some liquids which lie between 1.237 and 1.482 is the agreement with the general range of variation expected for organic liquids. In the case of the few inorganic liquids, the γ values are quite high being greater than 1.8. The C_V and γ values for some of the liquids investigated are obtained for the first time and are reported in Table I. Schaaffs (1951) has shown that Van der Waals' "b", and the molecular radii r of any molecule can be calculated from the relations.

$$b = \frac{M}{\rho}\left[1 - \frac{RT}{MV^2}\left\{\sqrt{1 + \frac{MV^2}{3RT}} - 1\right\}\right]$$

$$r = \sqrt[3]{\frac{3b}{16\pi N}}$$

where M = Molecular weight

ρ = density

T = Temperature in degrees absolute

V = Velocity of sound

R = Gas constant

b = Van der Waals' b
N = Avogadro number

r can also be calculated from the refractive index measurements by using the relation.

$$r = \sqrt[3]{\frac{3}{4\pi N}\,\frac{\mu^2-1}{\mu^2+2}\,\frac{M}{\rho}}$$

where μ = refractive index

The r values calculated by both these methods for most of the liquids investigated are presented in Table I. It will be seen that these values obtained by both these methods are in good agreement with each other. Although there are significant deviations in the case of the inorganic compounds like sulphur chloride, thionyl chloride and triphenyl phosphate, and also in azoxy benzene this discrepancy may be attributed partly to structural influences and partly to the impurity of chemicals.

From a study of the ultrasonic velocities in homologous series of organic liquids at 20°C Schaaffs has deduced the b values for some of the common elements having certain common linkages as for instance, —H —, >C<, >C = O = (C), etc. He has also calculated b values for certain organic groups which commonly occur in organic liquids. He has given different values for these groups depending on whether they are linked to aliphatic series or aromatic series. As b is found to be additive in nature, Schaaffs (1948) has calculated the b values for several organic liquids using the data for groups and atoms thus obtained, and compared these with the values calculated from ultrasonic velocities and found them to be in good agreement.

The authors have attempted an investigation on similar lines following however, a different procedure for the computation of Van der Waals' b. While Schaaffs has considered "b" values for atoms and atomic groups, the authors have considered the contribution as due to atoms and linkages like double, triple, and semipolar double bonds. The values thus obtained for various atoms linkages and ring structures using the data available in literature for some common organic liquids are given in the Table III. To check up the accuracy in the estimation of b values obtained for atoms and linkages, the b values for some other organic liquids are calculated from the ultrasonic velocity data and are compared with the computed values. This data is presented in Table III. Considering the fact that "b" is constitutive in nature to a certain extent and that the value of b for the same atom linked with different atoms has generally slightly different values, the agreement may be taken as quite satisfactory. Such of those differences which are significant may be attributed to the constitutive influences.

Using the "b" values for atoms, the b value for semipolar double bond is deduced from the calculated b value from ultrasonic velocities of the five liquids,

ethyl phosphate, methyl and ethyl sulphate, thionyl and sulphuryl chlorides, leaving the two liquids azoxy benzene and triphenyl phosphate. The interesting result was that the contribution of Van der Waals' b to semipolar linkage is negative and small. The negative value for b indicates that there is effectively a contraction in the volume of the molecule. This result is analogous to the negative value of parachor reported by Sugden (1930) and of molar sound velocity obtained by us. Since the structural formulae of azoxy benzene and triphenyl phosphate are quite large involving benzene ring and double bonds, the values of b estimated for them are not accurate. Perhaps that may be the reason why the contribution for semipolar bond in the two liquids turned up as positive.

Comparing the experimental values of b with the computed ones for the liquids investigated here, the agreement may be considered as gratifying for most of the liquids except naphthalene, phenyl salicylate, triphenyl phosphate, azo and axoxy benzenes. The large deviations observed in these liquids are due to constitutive effects which sometimes alter the values of the individual atomic contributions widely.

Since Schaaffs (1950) has attributed "b" values for groups instead of linkages it has limited application in computing the b value for a new liquid. According to his method the values for a large number of groups are to be known in order to compute the value of b for any new liquid, since there are so many possible combinations of atoms with various linkages, occurring normally in all the organic liquids. The author's method has wide application in the computation of "b" values for liquids but some times the computed values show large deviations from the experimental results due to consitutive influences.

REFERENCES

Baccaredda, M. and Gaicemini, A , 1945, *Ricera Scientifica*, **15**, 161.

Baccaredda, M. and Gaicemini, A., 1946, *Ricera Scientifica*, **16**, 611, 662.

Baccaredda, M. and Gaicemini, A., 1947, *Ricera Scientifica*, **17**, 1108.

Baccaredda, M. and Gaicemini, A., 1949, *Ricera Scientifica*, **19**, 358.

Baccaredda, M. and Gaicemini, A., 1950 *Ricera Scientifica*, **20**, 133.

Lagemann, R. T., 1948, *J. Chem. Phys.*, **16**, 247.

Lagemann, R. T., 1953, *J. Chem. Phys.*, **21**, 819.

Lagemann, R. T., 1948, *J. Am. Chem. Soc.*, **70**, 2994, 2996,

Lagemann, R. T., 1957, *J. Am. Chem. Soc.*, **78**, 3213, 5891.

Lagemann, R. T. and Dunbar, W. S., 1949, *J. Phys. Schem.*, **49**, 428.

Parthasarathy, S., 1935, *Proc. Ind. Acad. Sci.*, **2**, 497.

Parthasarathy, S., 1936, *Prob. Ind. Acad. Sci.*, **3**, 285, 518.

Parthasarathy, S., 1937, *Proc. Ind. Acad. Sci.*, **4**, 59, 213.

Rao, M. R., 1940, *Ind. J. Phys.*, **14**, 109.

Rao, M. R., 1941, *J. Chem. Phys.*, **9**, 682.

Schaaffs, W., 1948, *Zeits. Natur. for sch.*, **13A**, 396.

Schaaffs, W., 1950, *Zeits. Phys. Chem.*, **195**, 136.

Schaaff's W., 1951. *Zeits. Phys. Chem.*, **196**, 397, 413.

Sugden, S., 1930, Parachor and Valoney.